

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 231 239 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
14.08.2002 Bulletin 2002/33

(51) Int Cl.7: **C08L 27/12, C08L 53/00,
C08K 5/00**

(21) Application number: **02005410.2**

(22) Date of filing: **17.06.1998**

(84) Designated Contracting States:
BE DE FR GB IT NL

(30) Priority: **20.06.1997 IT MI971468**

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
98111124.8 / 0 885 928

(71) Applicants:
• **Ausimont S.p.A.**
20121 Milano (IT)
• **DaimlerChrysler AG**
70567 Stuttgart (DE)

(72) Inventors:
• **Gayer, Udo**
71732 Tamm (DE)

• **Schuh, Thomas**
71336 Waiblingen (DE)
• **Arcella, Vincenzo**
Novara (IT)
• **Albano, Margherita**
Milano (IT)

(74) Representative: **Sama, Daniele, Dr. et al**
Sama Patents,
Via G.B. Morgagni, 2
20129 Milano (IT)

Remarks:

This application was filed on 08 - 03 - 2002 as a
divisional application to the application mentioned
under INID code 62.

(54) **Fluorinated thermoplastic elastomers and articles therefrom**

(57) Manufactured articles obtainable from a com-
position consisting of :

1) 100 phr of a fluorinated thermoplastic elastomer
having a block structure with at least a fluorinated
polymeric segment of B type having elastomeric
properties and at least a fluorinated polymeric seg-
ment of A type having plastomeric properties,
whereby the fluorinated thermoplastic elastomer
comprises monomeric units which derive from an

iodinated olefin,
2) from 0.1 to 40 phr of a crosslinking agent able to
give peroxidic crosslinking of fluoroelastomers;
and subsequent irradiation of the manufactured ar-
ticle by GAMMA or BETA radiations.

EP 1 231 239 A1

Description

[0001] The present invention relates to fluorinated thermoplastic elastomers having improved sealing properties, in particular at high temperatures, at least up to 150°C.

[0002] As known, thermoplastic elastomers are block copolymers formed by at least a soft segment having elastomeric properties and by at least a hard segment having plastomeric properties. Such products combine therefore the properties typical of the conventional cured elastomers with those of the plastomers.

[0003] In comparison with the conventional elastomers, they do not require any curing process, wherefore they result easily processable and recyclable according to the techniques usually utilized for thermoplastic polymers, with clear both economic and ecologic advantages.

[0004] Fluorinated thermoplastic elastomers are known in the art. For instance in US patent 4,158,678, which is herein incorporated by reference, block fluorinated polymers, formed by alternate hard and soft segments, of which at least one is fluorinated, are described. Such products are obtained by radical polymerization of fluorinated monomers in the presence of an iodinated chain transfer agent having the formula RI_n , wherein R is a fluorinated radical, optionally containing chlorine, having from 1 to 8 carbon atoms, and n is 1 or 2, thus obtaining a first fluorinated polymeric segment, with elastomeric or plastomeric characteristics depending on the monomeric composition, having an iodine atom on one or both end groups. On such segment other different fluorinated or non fluorinated segments are then grafted, considering that the terminal iodine atoms are susceptible of radical attack and can therefore produce the growth of a new polymeric chain. It is thus possible to obtain, for instance, fluorinated thermoplastic elastomers of the A-B-A type, wherein A is a plastomeric segment (for instance a homopolymer or copolymer deriving from tetrafluoroethylene and/or vinylidenefluoride), while B is an elastomeric segment (for instance a tetrafluoroethylene/vinylidene fluoride/hexafluoropropene copolymer). Other thermoplastic elastomers of this kind are described in EP 444,700.

[0005] A limit of such products consists in that the mechanical and elastic properties easily worsen when the temperature rises and result quite unsatisfactory already at 50°C. In particular the compression set values are high, such as to make the products unsuitable to the manufacture of sealing elements (for instance shaft seals or O-rings or the like) to be employed at high temperatures, as requested by the motor, aerospace, plant industry.

[0006] Fluorinated thermoplastic elastomers, having improved mechanical and elastic properties by the introduction in the polymeric chain of small amounts of a bis-olefin, are also known from USP 5,612,419. The resulting products are in particular characterized by improved mechanical properties and by particularly low compression set values in comparison with the fluorinated thermoplastic elastomers of the patents previously described.

[0007] New fluorinated thermoplastic elastomers are also known from EP patent 683,186, which have mechanical and elastomeric properties similar to the products of US patent 5,612,419 but having in the chain instead of the bis-olefin, small amounts of a fluorinated olefin containing a terminal iodine atom.

[0008] However the sealing properties of the products mentioned above are not satisfactory at high temperatures, in particular at the temperature of 150°C.

[0009] The need was felt to have available thermoplastic elastomers with improved sealing properties at high temperatures, in particular the compression set (C set).

[0010] An object of the present invention are manufactured articles obtainable from a composition consisting essentially of:

1) 100 phr of a fluorinated thermoplastic elastomer having a block structure with at least a fluorinated polymeric segment of type B having elastomeric properties and at least a fluorinated polymeric segment of type A having plastomeric properties,

2) from 0.1 to 40 phr of a crosslinking agent able to give peroxidic crosslinking of fluoroelastomers;

and subsequent radiation of the manufactured article by GAMMA radiations, from 1 to 50 Mrad, preferably from 1 to 30 Mrad, or BETA radiations from 10 to 500 KGy, preferably from 10 to 300 KGy.

Preferably the amount of the component 2) ranges from 1 to 10 phr.

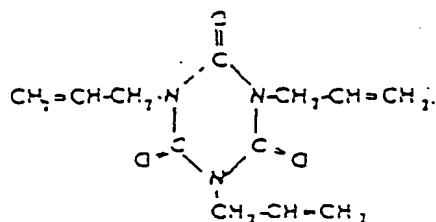
[0011] The composition of the invention can contain other additives such as fillers, for instance carbon black, silica, stabilizers, antioxidants, pigments, thickeners, plastifiers, etc. The amount of these additives generally ranges from 0.5 to 40 phr, preferably from 1 to 20 phr.

[0012] The crosslinking agents which can be used are for instance: triallyl-cyanurate; triallyl-isocyanurate (TAIC); tris(diallylamine)-s-triazine; triallylphosphite; N,N-diallyl-acrylamide; fluorinated bis-olefins as defined hereinafter, N,N'-bisallylbicyclo-oct-7-ene-disuccinimide (BOSA); N,N,N'-tetraallyl-malonamide; trivinyl-isocyanurate; 2,4,6-trivinyl-methyltrisiloxane, etc. A crosslinking agent or a mixture of the crosslinking agents above mentioned can be utilized.

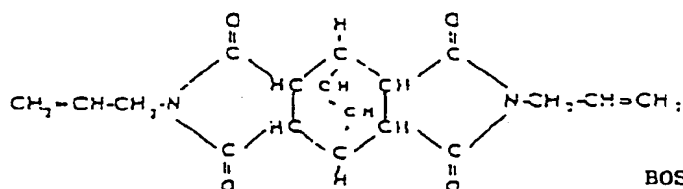
[0013] It has been found that the compositions of the invention subjected to treatment with BETA or GAMMA radiations give a remarkable increase of the sealing properties, even at high temperatures up to 150°C. The effect is particularly meaningful when the thermoplastic elastomer contains as plastomeric block the one essentially formed by

PVDF. In this case, it is sufficient a very low amount of radiations, for instance 1 Mrad of GAMMA rays, to obtain the improved sealing properties.

[0014] As preferred crosslinking agents, TAIC, 1,6 divinylperfluorohexane (bis-olefin), BOSA can be mentioned, which have the following structures:

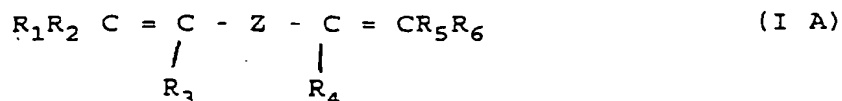


TAIC

1,6 DIVINYLPERFLUOROHXANE
(BO)

BOSA

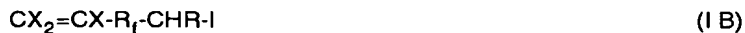
[0015] The fluorinated thermoplastic elastomer consists essentially of a block structure with at least a fluorinated polymeric segment of B type having elastomeric properties and at least a fluorinated polymeric segment of A type having plastomeric properties, optionally with at least one of the segments of A or B type, preferably B, wherein monomeric units are present deriving from a bis-olefin having the general formula:



wherein:

$\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4, \text{R}_5, \text{R}_6$, equal to or different from each other, are H or alkyls $\text{C}_1\text{-C}_5$; Z is an alkylene or cycloalkylene radical $\text{C}_1\text{-C}_{18}$, linear or branched, optionally containing oxygen atoms, preferably at least partially fluorinated, or a (per)fluoropolyoxyalkylenic radical.

[0016] In at least one among the A or B segment type, preferably B, monomeric units deriving from at least an iodinated olefin instead of the bis-olefin can be present, having the formula:

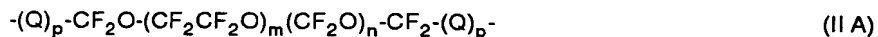


wherein:

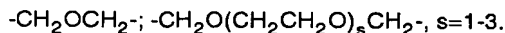
X is -H, -F, or - CH_3 ; R is -H or - CH_3 ; R_1 is a (per)fluoroalkylenic, linear or branched radical, optionally containing one or more atoms of ether oxygen, or a (per)fluoropolyoxyalkylenic radical.

[0017] In the formula (I A), Z is preferably a perfluoroalkylenic radical C₄-C₁₂, whereas R₁, R₂, R₃, R₄, R₅, R₆ are preferably hydrogen.

[0018] When Z is a (per)fluoropolyoxyalkylenic radical, it has preferably the formula:



wherein: Q is an alkylenic or oxyalkylenic radical C₁-C₁₀; p is 0 or 1; m and n are integers such that the m/n ratio is in the range 0.2-5 and the molecular weight of said (per)fluoropolyoxyalkylenic radical is in the range 500 and 10,000, preferably 1,000-4,000. Preferably, Q is selected from:



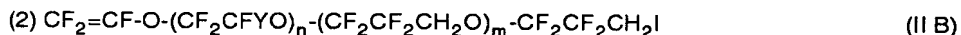
[0019] The bis-olefins of formula (IA) wherein Z is an alkylenic or cycloalkylenic radical can be prepared according to what described, for instance, by I.L. Knunyants et al in Izv. Akad. Nauk. SSSR, Ser. Khim., 1964(2), 384-6, while the bis-olefins containing the (per)fluoropolyoxyalkylenic sequences of formula (II) are described in US patent 3,810,874.

[0020] The amount of units deriving from such bis-olefins is generally in the range 0.01-1.0%, preferably 0.03-0.5%, still more preferably 0.05-0.2% by mole, calculated with respect to the total amount of the other monomers of the elastomer or plastomer.

[0021] Iodinated olefins according to the formula (I B) can be selected in particular from the following classes:



wherein: R is -H or -CH₃; Z is a (per)fluoroalkylenic radical C₁-C₁₈, linear or branched, optionally containing one or more atoms of ether oxygen, or a (per)fluoropolyoxyalkylenic radical;



wherein: Y is -F or -CF₃; m is an integer in the range 0-5; n is 0, 1 or 2.

[0022] As for the formula (II B), Z is preferably a perfluoroalkylenic radical C₄-C₁₂, or a (per)fluoropolyoxyalkylenic radical, as defined in formula (II A).

[0023] The unit amount deriving from the iodinated olefins of formula (I B) is generally in the range 0.01-1.0 by mole, preferably 0.03-0.5 by mole, still more preferably 0.05-0.2 by mole per 100 moles of the other basic monomeric units of the elastomer or of the plastomer.

[0024] The bis-olefins of formula (I A) and the olefins of formula (I B) are described respectively in US patent 5,612,419 and EP 683,186 incorporated herein by reference.

[0025] The fluorinated elastomer and the fluorinated plastomer are obtained by (co)polymerization of olefinic monomers. With fluorinated olefinic monomers are meant all the fluorinated products having at least a double bond C=C, optionally containing hydrogen and/or chlorine and/or bromine and/or iodine and/or oxygen, capable of producing (co) polymers in the presence of radical initiators. Among them we can cite: perfluoroolefins C₂-C₈, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP), hexafluoroisobutene; hydrogenated fluoroolefins C₂-C₈, such as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, perfluoroalkylethylene CH₂=CH-R_f, wherein R_f is a perfluoroalkyl C₁-C₆; chloro- and/or bromo-and/or iodo-fluoroolefins C₂-C₈, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluoroalkylvinylethers (PAVE) CF₂=CFOR_f, wherein R_f is a (per)fluoroalkyl C₁-C₆, for instance trifluoromethyl, bromodifluoromethyl or pentafluoropropyl; (per)fluoro-oxyalkylvinylethers CF₂=CF-OR_f, wherein R_f is a (per)fluoro-oxyalkyl C₁-C₁₂ having one or more ether groups, for instance perfluoro-2-propoxy-propyl; perfluorodioxoles.

[0026] Such fluorinated olefinic monomers can also be copolymerized with non fluorinated olefins C₂-C₈, such as ethylene, propylene, isobutylene.

[0027] The type B segments (elastomeric) can in particular be selected from the following classes (compositions expressed as % by mole):

(1) VDF-based copolymers, wherein VDF is copolymerized with at least a comonomer selected from: perfluoroole-

fins C₂-C₈; chloro- and/or bromo- and/or iodo-fluoroolefins C₂-C₈; (per)fluoroalkylvinylethers (PAVE) or (per)fluoroalkoxyalkylvinylethers above defined; non fluorinated olefins (OI) C₂-C₈; typical compositions are the following:

(a) VDF 45-85%, HFP 15-45%, TFE 0-30%; (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%; (c) VDF 20-30%, OI 10-30%, HFP and/or PAVE 18-27%, TFE 10-30%;

(2) TFE-based copolymers, wherein TFE is copolymerized with at least a comonomer selected from: (per)fluoroalkylvinylethers (PAVE) or (per)fluoroalkoxyalkylvinylethers above defined; hydrogenated fluoroolefins C₂-C₈; fluoroolefins C₂-C₈ containing chlorine and/or bromine and/or iodine atoms; non fluorinated olefins (OI) C₂-C₈; typical compositions are the following: (a) TFE 50-80%, PAVE 20-50%; (b) TFE 45-65%, OI 20-55%, VDF 0-30%; (c) TFE 32-60%, OI 10-40%, PAVE 20-40%.

[0028] The type A segments (plastomeric) can in particular be selected from the following classes (compositions expressed as % by mole):

(1) polytetrafluoroethylene or modified polytetrafluoroethylene containing small amounts, generally in the range 0.1-3%, preferably lower than 0.5%, of one or more comonomers such as, for instance: HFP, PAVE, VDF, hexafluoroisobutene, CTFE, perfluoroalkylethylenes;

(2) TFE thermoplastic polymers containing from 0.5 to 8% of at least a PAVE, such as, for instance, TFE and perfluoropropylvinylether and/or perfluoromethylvinylether copolymers, or also TFE/perfluoroalkylethylene copolymers;

(3) TFE thermoplastic polymers containing from 2 to 20% of a perfluoroolefin C₃-C₈, such as, for instance, FEP (TFE/HFP copolymer), to which other comonomers having a vinylether structure CF₂=CF-OR_f or CF₂=CF-OR_f defined as above can be added in small amounts (lower than 5%);

(4) TFE or CTFE copolymers (40-60%) with ethylene, propylene or isobutylene (40-60%), optionally containing as third comonomer a (per) fluoroolefin C₃-C₈ or a PAVE, in amounts in the range 0.1-10%;

(5) polyvinylidene fluoride or modified polyvinylidene fluoride containing small amounts, generally comprised between 0.1 and 10%, of one or more fluorinated comonomers, such as hexafluoropropene, tetrafluoroethylene, trifluoroethylene.

[0029] The thermoplastic polymers of the classes above indicated, and in particular the TFE-based polymers, can be modified with (per)fluorinated dioxoles, according to the patents US-3,865,845, US-3,978,030, EP-73,087, EP-76,581, EP-80,187.

[0030] It has been found by Applicants that the mechanical and sealing properties of the manufactured articles, after GAMMA or BETA irradiation, can be further improved by subjecting the articles so obtained to a thermal treatment for about 1-6 hours at a temperature lower of about 10°-30°C with respect to the melting temperature of the plastomer. This treatment can be called annealing.

[0031] Applicants have also found that the above properties are further increased if the above thermal treatment is carried on the manufactured articles before subjecting them to GAMMA or BETA irradiation.

[0032] The present invention will be now better illustrated by the following working examples which have a merely indicative purpose but not limitative of the scope of the present invention.

EXAMPLE 1

PREPARATION OF THE THERMOPLASTIC FLUOROELASTOMER (FTPE) 1 CONTAINING PVDF AS PLASTOMERIC BLOCK A

[0033] The thermoplastic fluoroelastomer having the structure A-B-A was prepared according to Example 1 of US Patent 5,612,419 but by modifying the VDF and TFE monomer feeding composition and using perfluoromethylvinylether (MVE) instead of HFP, to obtain a final composition of block B (¹⁹F NMR analysis):

VDF 61% by mole

MVE 19% by mole

TFE 20% by mole

Moreover the polymer contains:

Bis-olefin 0.07% by mole.

The polymer Mooney viscosity is equal to 12 Mooney points (A-STM D 1546).

EP 1 231 239 A1

The final thermoplastic fluoroelastomer contains, in addition to the elastomeric B phase above specified, also a thermoplastic phase based on PVDF in the amount of 20% by weight on the total amount of the two phases and obtained as described in Example 1 of the above mentioned patent.

5 [0034] The FTPE 1 melting temperature is 160°C.

[0035] The material results to be under the form of thick powder coming from the coagulation and washing of the polymerization latex.

EXAMPLE 2

10

FTPE 2 PREPARATION CONTAINING E/TFE/MVE AS PLASTOMERIC

BLOCK A

15 [0036] The thermoplastic fluoroelastomer with A-B-A structure was prepared as in Example 1 but modifying the amounts of the fed monomers so that to obtain the compositions indicated below.

[0037] In particular the fluoroelastomeric segment B has the following composition (¹⁹F NMR analysis):

20 VDF 57% by mole

MVE 23% by mole

TFE 20% by mole

Bis-olefins 0.11% by mole

Mooney viscosity = 36

25 The final thermoplastic fluoroelastomer contains, in addition to the elastomeric B phase, also a thermoplastic phase which instead of the PVDF of Example 1, has the following molar composition:

ethylene	E 41% by mole
tetrafluoroethylene	TFE 50% by mole
perfluoromethylvinylether	MVE 9% by mole

30

The amount of plastomeric phase is 25% by weight on the total amount of the two phases.

[0038] The FTPE 2 second melting temperature is 180°C.

35 [0039] The material results to be under the form of a thick powder coming from the coagulation and washing of the polymerization latex.

EXAMPLE 1A

40 [0040] 100 phr of FTPE 1 polymer are mixed in a laboratory single screw extruder with 3 phr of TAIC (triallylisocyanurate) and then pelletized with the same equipment.

[0041] With the obtained formulation, 100x100x2 mm specimen have been compression molded for the mechanical tests: M100 means 100% elongation modulus, M200 means 200% elongation modulus, CR means stress at break, AR means elongation at break, Shore A hardness. Moreover disks have been molded (13 mm of diameter and 6 mm of thickness) for compression set tests at high temperature carried out according to VDA 675 216-B standard or ASTM D 395 method B. The sheets and the disks have been then irradiated with GAMMA rays (Co-60), with dosages 1, 5 and 10 Mrad.

45 [0042] The results are reported in Table 1 in which the comparison is carried out also with the pelletized polymer not containing crosslinking coagents and not submitted to crosslinking with radiations.

50

TABLE 1

	after molding in press (comparison)	after 3 phr TAIC		
		1Mrad	5 Mrad	10Mrad
Mech. prop. after press				

55

EP 1 231 239 A1

TABLE 1 (continued)

		after molding in press (comparison)	after 3 phr TAIC		
			1Mrad	5 Mrad	10Mrad
180°C x 11min (ASTM D 412-83)					
M 100	(MPa)	2.3	7.2	12.5	15.3
M 200	"	3	11.5	-	-
CR	"	3.1	14.9	18.2	19
AR	%	231	281	167	131
Hardness	points	58	79	86	87
C disk set (VDA*) 150°C x (22+2)h		101	78	72	70
%					

* The VDA standard is used in some sectors of automotive field as it results much more severe and meaningful of the corresponding ASTM method. In the case of the comparative Example of Table 1 the C set value according to ASTM at 150°Cx24h on O-ring is equal to 60%.

EXAMPLE 1B

[0043] One proceeds as in Example 1A except that the specimen and the disks are irradiated with BETA rays (4,5 MeV), with dosages 10.9; 28.4; 60.4; 120.9 KGy (1 Mrad = 10 KGy)

[0044] The results are reported in Table 2 and the compression set data at the different temperatures in Table 3.

TABLE 2:

Mechanical properties				
	CR (MPa)	AR (%)	M50 (MPa)	M100 (MPa)
10.9 KGy	10.5	299	1.8	3.6
28.4 "	12.7	208	2.4	5.5
60.4 "	12.5	161	2.9	7.4
120.9 "	12.9	131	3.6	9.6

TABLE 3:

Compression set according to VDA standard			
	100°C (%)	125°C (%)	150°C (%)
10.9 KGy	61	72	
28.4 "	48	58	
60.4 "	41		66
120.9 "	36		60

EXAMPLE 2A

[0045] The FTPE 2 polymer is subdivided in 3 parts, each of them is mixed by means of a laboratory single screw extruder with different kinds of coagents in amounts of 3 phr. The coagents used are TAIC, BOSA and 1,6 divinylperfluorohexane (BISOLEFIN) (indicated with BO in the Tables) . With the formulations obtained, 100x100x2 mm specimen have been compression molded for mechanical tests. Moreover disks have been compression molded for compression set tests at high temperature.

[0046] The specimen and the disks have then been irradiated with GAMMA rays (Co-60) with a 5 Mrad dosage.

[0047] The results are reported in Table 4 in which the comparison is carried out also with the pelletized polymer not containing crosslinking coagents. Mechanical properties and the compression set for all the samples are carried out also on non irradiated specimen and disks.

EP 1 231 239 A1

TABLE 4

		COMPARATIVE	3 phr BOSA	3 phr BISOLEFIN	3 phr TAIC
5	Mech. prop. after press 180 °C x 11 min (ASTM D412-83)				
	M 100 (Mpa)	2.8	3	2.4	2.9
	C.R. "	6.2	7.7	6.9	7
10	A.R. %	588	573	571	570
	Hardness points	68	71	66	69
	C.set at 150 °C on disks				
	ASTM 24h %	98	102	99	101
15	VDA(22+2)h %	108	110	112	112
	Mech. prop after radiation with 5 Mrad of GAMMA rays				
	M 100 (Mpa)	2.6	3.6	2.2	4.3
	C.R. "	7.8	12.7	7.7	14.1
20	A.R. %	422	383	556	283
	Hardness points	67	71	62	74
	C. set at 150°C on disks after radiation of 5 Mrad of GAMMA rays				
25	ASTM 24h %	75	66	87	59
	VDA(22+2)h %	102	95	93	98

EXAMPLE 4

[0048] One proceeds as in Example 3 except that the sheets and the disks are radiated with BETA rays (4,5 MeV), with dosages 50, 250, 500 KGy (1 Mrad = 10 KGy).

[0049] The mechanical properties are reported in Tab. 5 and the compression set data measured at the different temperatures in Tab. 6.

TABLE 5:

Mechanical properties					
		C.R. (MPa)	A.R. (%)	M 50 (MPa)	M 100 (MPa)
	BO				
	Not radiated	6.9	671	-	2.4
40	50 KGy	11.1	321	2.3	3.5
	250 "	10.1	160	2.8	4.9
	500 "	6.8	102	3.6	6.8
45	BOSA				
	Not radiated	7.7	573	-	3.0
	50 KGy	13.8	356	2.6	3.9
	250 "	13.5	141	4.3	8.0
50	500 "	9.9	78	6.0	-
	TAIC				
	Not radiated	7.0	570	-	2.9
	50 KGy	14.4	238	3.0	4.9
55	250 "	8.7	89	5.0	-
	500 "	8.8	66	6.8	-

TABLE 6:

Compression set VDA (22+2) h			
		100 °C (%)	125°C (%)
50 250 500	BO KGy "	88 61 58	93 71 64
	BOSA KGy "	83 63 62	100 79 72
	TAIC KGy "	79 63 64	90 73 73

Claims

1. Manufactured articles obtainable from a composition consisting of:

1) 100 phr of a fluorinated thermoplastic elastomer having a block structure with at least a fluorinated polymeric segment of B type having elastomeric properties and at least a fluorinated polymeric segment of A type having plastomeric properties, whereby in at least one among the A or B type segments monomeric units are present which derive from at least an iodinated olefin having the formula:



wherein:

X is -H, -F, or -CH₃; R is -H or -CH₃; R_f is a (per)fluoroalkylenic, linear or branched radical, optionally containing one or more atoms of ether oxygen, or a (per)-fluoropolyoxyalkylenic radical;

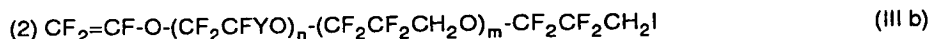
2) from 0.1 to 40 phr of a crosslinking agent able to give peroxidic crosslinking of fluoro-elastomers; and subsequent radiation of the manufactured article by GAMMA radiations, from 1 to 50 Mrad, or BETA radiations from 10 to 500 KGy.

2. Manufactured articles according to claim 1 wherein the component 2) amount ranges from 1 to 10 phr.
3. Manufactured articles according to claims 1 and 2 wherein the composition contains additives such as fillers, stabilizers, antioxidants, pigments, thickeners and plastifiers.
4. Manufactured articles according to claims 1-3 wherein the crosslinking agents are selected from 1,6-divinylperfluorohexane; triallyl-cyanurate; triallylisocyanurate (TAIC); tris(diallylamine)-s-triazine; triallylphosphite; N,N-diallyl-acrylamide; fluorinated bis-olefins, N,N' bisallylbicycle-oct-7-ene-disuccinimide (BOSA); N,N,N',N'-tetraallyl-malonamide; trivinyl-isocyanurate; and 2,4,6-trivinyl-methyltrisiloxane.
5. Manufactured articles according to claim 4, wherein the crosslinking agents are selected from TAIC, 1,6 divinylperfluorohexane, and BOSA.
6. Manufactured articles according to claim 5, wherein the iodinated olefin is present in the fluorinated polymeric segment of type B having elastomeric properties.

7. Manufactured articles according to claim 6, wherein the iodinated olefin is selected from the following classes:



wherein: R is -H or -CH₃; Z is a (per)fluoroalkylenic radical C₁-C₁₈, linear or branched, optionally containing one or more atoms of ether oxygen, or a (per)fluoropolyoxyalkylenic radical;



wherein: Y is -F or -CF₃; -m is an integer in the range 0-5; n is 0, 1 or 2.

8. Manufactured articles according to claim 7 wherein the amount of units deriving from the iodinated olefin is generally in the range 0.01-1.0 by moles per 100 moles of the other monomeric units of the elastomer or the plastomer.

9. Manufactured articles according to claim 8 wherein the fluorinated elastomer and the fluorinated plastomer blocks are obtained by (co)polymerization of fluorinated olefinic monomers having at least a double bond C=C, optionally containing hydrogen and/or chlorine and/or bromine and/or iodine and/or oxygen, able to produce (co)-polymers in the presence of radical initiators.

10. Manufactured articles according to claim 9 wherein the fluorinated olefinic monomers are selected from: perfluoroolefins C₂-C₈, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP), and hexafluoroisobutene; hydrogenated fluoroolefins C₂-C₈, such as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, and perfluoroalkylethylene CH₂=CH-R_f, wherein R_f is a perfluoroalkyl C₁-C₆; chloro- and/or bromo- and/or iodo-fluoroolefins C₂-C₈, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluoroalkylvinylethers (PAVE) CF₂=CFOR_f, wherein R_f is a (per)-fluoroalkyl C₁-C₆, such as trifluoromethyl, bromodifluoromethyl or pentafluoropropyl; (per)fluorooxyalkylvinylethers CF₂=CFOX, wherein X is a (per)fluorooxyalkyl C₁-C₁₂ having one or more ether groups, such as perfluoro-2-propoxy-propyl; and perfluorodioxoles.

11. Manufactured articles according to claim 10 wherein the fluorinated olefinic monomers are copolymerized in the presence of non fluorinated olefins C₂-C₈, such as ethylene, propylene, isobutylene.

12. Manufactured articles according to claim 11 wherein the B type segments (elastomeric) are selected from the following classes:

(1) VDF-based copolymers, wherein VDF is copolymerized with at least a comonomer selected from: perfluoroolefine C₂-C₈; chloro- and/or bromo- and/or iodo-fluoroolefins C₂-C₈; (per)fluoroalkylvinylethers (PAVE) or (per)fluorooxyalkylvinylethers above defined; non fluorinated olefins (OI) C₂-C₈; and

(2) TFE-based copolymers, wherein TFE is copolymerized with at least a comonomer selected from: (per)fluoroalkylvinylethers (PAVE) or (per)fluorooxyalkylvinylethers above defined; hydrogenated fluoroolefins C₂-C₈; fluoroolefins C₂-C₈ containing chlorine and/or bromine and/or iodine atoms; non fluorinated olefins (OI) C₂-C₈;

13. Manufactured articles according to claim 12 wherein the type A segments (plastomeric) are selected from the following classes:-

(1) polytetrafluoroethylene or modified polytetrafluoroethylene with amounts in the range 0.1-3%, preferably lower than 0.5%, of one or more comonomers such as HFP, PAVE, VDF, hexafluoroisobutene, CTFE, perfluoroalkylethylenes;

(2) TFE thermoplastic polymers containing from 0.5 to 8% of at least a PAVE, such as TFE/perfluoropropylvinylether copolymers and/or TFE/perfluoromethylvinylether copolymers, or also TFE/perfluoroalkylethylene copolymers;

(3) TFE thermoplastic polymers containing from 2 to 20% of a perfluoroolefin C₃-C₈, such as FEP (TFE/HFP copolymer), to which amounts lower than 5% of other comonomers having a vinylether structure CF₂=CF-OR_f or CF₂=CF-OX above defined can be added;

(4) TFE or CTFE copolymers (40-60%) with ethylene, propylene or isobutylene (40-60%), optionally containing

as third comonomer a (per)fluoroolefin C₃-C₈ or a PAVE, in amounts in the range 0.1-10%;
 (5) polyvinylidenefluoride or modified polyvinylidenefluoride with amounts in the range 0.1-10%, of one or more
 fluorinated comonomers, such as hexafluoropropene, tetrafluoroethylene, trifluoroethylene.

14. Manufactured articles according to claim 13 wherein the thermoplastic polymers are modified with (per)fluorinated dioxoles.

15. Manufactured articles according to claim 14 wherein the manufactured articles before being subjected to irradiation treatment are subjected to a thermal treatment for 1-6 hours at a temperature 10°-30°C lower than the melting point of plastomer A.

16. Manufactured articles according to claim 15 wherein the manufactured articles after being subjected to irradiation treatment are subjected to a thermal treatment for 1-6 hours at a temperature 10°-30°C lower than the melting point of plastomer A.

17. Manufactured articles according to claim 12 wherein the VDF-based copolymers are selected from (compositions expressed as % by moles): (a) VDF 45-85%, HFP 15-45%, 0-30% TFE; (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%; (c) VDF 20-30%, OI 10-30%, HFP and/or PAVE 18-27%, TFE 10-30%; and the TFE-based copolymers are selected from (compositions expressed as % by moles): (a) TFE 50-80%, PAVE 20-50%; (b) TFE 45-65%, OI 20-55%, 0-30% VDF; (c) TFE 32-60%, OI 10-40%, PAVE 20-40%.

18. Use of a composition consisting of:

1) 100 phr of a fluorinated thermoplastic elastomer having a block structure with at least a fluorinated polymeric segment of B type having elastomeric properties and at least a fluorinated polymeric segment of A type having plastomeric properties, whereby in at least one among the A or B type segments monomeric units are present which derive from at least an iodinated olefin having the formula:



wherein:

X is -H, -F, or -CH₃; R is -H or -CH₃; R_f is a (per)fluoroalkylenic, linear or branched radical, optionally containing one or more atoms of ether oxygen, or a (per)-fluoropolyoxyalkylenic radical;

2) from 0.1 to 40 phr of a crosslinking agent able to give peroxidic crosslinking of fluoro-elastomers; for the preparation of manufactured articles having improved sealing properties at high temperatures, by irradiating the composition with GAMMA radiations, from 1 to 50 Mrad, or BETA radiations from 10 to 500 KGy.

19. Use according to claim 18 wherein the component 2) amount ranges from 1 to 10 phr.

20. Use according to claim 18 wherein the composition contains additives such as fillers, stabilizers, antioxidants, pigments, thickeners and plastifiers.

21. Use according to claim 18 wherein the crosslinking agents are selected from 1,6-divinylperfluorohexane; triallyl-cyanurate; triallyl-isocyanurate (TAIC); tris(diallylamine)-s-triazine; triallylphosphite; N,N-diallyl-acrylamide; fluorinated bis-olefins, N,N'-bisallylbicyclo-oct-7-ene-disuccinimide (BOSA); N,N,N',N'-tetraallyl-malonamide; trivinyl-isocyanurate; and 2,4,6-trivinyl-methyltrisiloxane.

22. Use according to claim 21, wherein the crosslinking agents are selected from TAIC, 1,6 divinylperfluorohexane and BOSA.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 00 5410

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D, Y	EP 0 683 186 A (AUSIMONT SPA) 22 November 1995 (1995-11-22) * claim 1 *	1-22	C08L27/12 C08L53/00 C08K5/00
Y	WO 91 02770 A (RAYCHEM CORP) 7 March 1991 (1991-03-07) * claims 1,3,5 *	1-22	
Y	EP 0 132 834 A (DAIKIN IND LTD) 13 February 1985 (1985-02-13) * page 5, line 1-19; claims 1,2 *	1-22	
A	WO 94 02185 A (ADVANCED CARDIOVASCULAR SYSTEM) 3 February 1994 (1994-02-03) * page 5, line 5-8 * * page 6, line 19-26 * * page 7, line 19 - page 8, line 10 *	1-22	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08L C08F C08K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 June 2002	Examiner Rodriguez, L
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 B2 (P04011)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 00 5410

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-06-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0683186	A	22-11-1995	IT	1269513 B	01-04-1997
			AT	158000 T	15-09-1997
			CA	2149581 A1	19-11-1995
			CN	1117502 A	28-02-1996
			DE	69500675 D1	16-10-1997
			DE	69500675 T2	19-02-1998
			EP	0683186 A1	22-11-1995
			ES	2108510 T3	16-12-1997
			JP	7316246 A	05-12-1995
			RU	2158273 C2	27-10-2000
			US	5605971 A	25-02-1997
WO 9102770	A	07-03-1991	US	5057345 A	15-10-1991
			AT	129271 T	15-11-1995
			CA	2062727 A1	18-02-1991
			DE	69023142 D1	23-11-1995
			DE	69023142 T2	20-06-1996
			EP	0487559 A1	03-06-1992
			JP	4507430 T	24-12-1992
			WO	9102770 A1	07-03-1991
EP 0132834	A	13-02-1985	JP	1699098 C	28-09-1992
			JP	3059937 B	12-09-1991
			JP	60028444 A	13-02-1985
			EP	0132834 A2	13-02-1985
			US	4603175 A	29-07-1986
WO 9402185	A	03-02-1994	WO	9402185 A1	03-02-1994

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

This Page Blank (uspto)